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## EUROPEAN PATENT APPLICATION

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⑤④ Film-forming thermoplastic elastomeric polymer compositions.

⑤⑦ There are disclosed film-forming polymer blends useful for the production of tubular blown film comprising EPM or EPDM elastomers, ethylene-vinyl acetate copolymers and a hydrocarbon oil plasticizer. The films exhibit resiliency and elasticity and high melt flow properties.

**EP 0 032 804 A2**

1           This invention relates to the thermoplastic elas-  
2   tomer polymer blends which have film-forming capabilities.  
3   More particularly, the invention relates to a film-forming  
4   blend of EPM or EPDM elastomer, thermoplastic ethylene-  
5   vinyl acetate copolymer resin and a hydrocarbon process  
6   oil, the blended composition being capable of processing in  
7   a tubular blown film apparatus.

8           Compositions containing EPM or EPDM elastomers,  
9   ethylene-vinyl acetate and hydrocarbon extender oils are  
10   known and are disclosed, for example, in German published  
11   Application 2822815 (1975) and Chemical Abstracts 90:169998a  
12   of Mitsui Petrochemical Industries, Ltd., the compositions  
13   being cured with a peroxide to form extrudable or injection  
14   moldable pellets.

15           Also, U.S. Patent 3,941,859 issued to Batiuk et  
16   al on March 2, 1976, discloses blends of EPDM polymers,  
17   polyethylene and ethylene-vinyl acetate, which are not  
18   cured and which are said to be useful for tubing, liners  
19   and molded products. The use of plasticizers and extenders  
20   is noted with the comment that such materials can detract  
21   from tensile strength.

22           In British Application 2,012,281, A. Romey et al  
23   disclose a mixture of olefin copolymer rubber, liquified  
24   coal product and ethylene-vinyl acetate useful as sealants  
25   and coatings.

26           In U.S. Patent 4,102,855, issued to Kuan et al  
27   on July 25, 1978, there are disclosed blends of EPDM poly-  
28   mers, ethylene-vinyl acetate copolymers and poly alpha-  
29   methyl styrene which are processable compositions useful  
30   for making injected moldable structural components.

31           These references, while disclosing various blends  
32   containing some components used in the present invention,  
33   all fail to disclose film-forming compositions and films  
34   made therefrom as disclosed herein.

35           In accordance with the present invention, there  
36   is provided a film-forming thermoplastic elastomeric poly-  
37   mer blend composition consisting essentially of:

1 (a) about 25 to 55 parts by weight of an EPM or  
2 EPDM elastomer;

3 (b) about 35 to 55 parts by weight of ethylene-  
4 vinyl acetate copolymer resin containing about 9 to 40% by  
5 weight vinyl acetate; and

6 (c) about 15 to 25 parts by weight of a normally  
7 liquid hydrocarbon process oil, the oil being an aromatic,  
8 highly aromatic, naphthenic or paraffinic process extender  
9 oil, the blend composition containing at least 4.5% by  
10 weight of vinyl acetate based upon the weight of the total  
11 composition and the blend composition having a melt index  
12 at 190°C of about 0.5 to 15.0 gm./10 min.

13 A further embodiment of the present invention  
14 comprises the aforesaid (a), (b) and (c) ingredients, to-  
15 gether with (d) about 0 to 30 parts by weight of calcium  
16 carbonate as a filler and opacifying agent and (e) about  
17 0.5 to 2% by weight of a film processing slip agent or ab-  
18 herent based upon the weight of the total blend composition.

19 The elastomeric polymer component to be used in  
20 the composition of the present invention may be either an  
21 EPM (ASTM D-1418-72a designation for an ethylene-propylene  
22 elastomer copolymer), or an EPDM (ASTM D-1418-72a designa-  
23 tion for an ethylene-propylene-diene elastomer terpolymer).  
24 Both EPM and EPDM are equally suitable for use in the pres-  
25 ent invention. Since no curing is involved, the noncon-  
26 jugated diene present in the EPDM does not add to or de-  
27 tract from the performance of the compositions prepared ac-  
28 cording to the present invention. Typical nonconjugated  
29 dienes employed in EPDM polymers are hexadiene, dicyclo-  
30 pentadiene, ethylidene norbornene, methylene norbornene,  
31 propylidene norbornene and methyltetrahydroindene. EPDM's  
32 with ethylidene norbornene have been used in formulating  
33 compositions of the present invention. The EPM and EPDM  
34 polymers used in the present invention should have an  
35 ethylene content of about 55 to about 70 weight percent,  
36 preferably about 60 to 70 weight percent, and a Mooney vis-  
37 cosity (ML 1 + 8 at 260°F) between about 25 and 80. Oil-

1 extended EPM and EPDM polymers may also be used if their  
2 Mooney viscosity falls within this range in the oil-extended  
3 state.

4           The ethylene-vinyl acetate copolymers useful in  
5 the present invention are those thermoplastic resins having  
6 a vinyl acetate content between about 9% and 28% by weight.  
7 Sufficient ethylene-vinyl acetate copolymer resin must be  
8 employed so that the final overall blended composition has  
9 a vinyl acetate content of at least 4.5% by weight. This  
10 level of vinyl acetate has been found required to act in  
11 combination with the plasticizing oil to impart a suffi-  
12 cient melt index to the film to aid in accommodating the  
13 oil without bleeding and to impart a high level of stretch  
14 and recovery to the film.

15           Hydrocarbon oils useful in the present invention  
16 function as process aids whose activity is uniquely enhanced  
17 in the presence of vinyl acetate copolymers, as plasticiz-  
18 ers producing low modulus and enhanced elasticity in the  
19 solid state and those useful are the normally liquid hydro-  
20 carbon processing and extender oils (ASTM D 2226) categor-  
21 ized as aromatic, highly aromatic, naphthenic and paraf-  
22 finic process oils of a medium viscosity range. Oils sold  
23 under the trademarks "Flexon" and "Sunpar" have been found  
24 especially useful.

25           The blended composition of the present invention  
26 exhibits excellent melt strength, and therefore may be man-  
27 ufactured into films using the conventional tubular blown-  
28 bubble extrusion process. In this process, which is widely  
29 used for the manufacture of polyethylene film, a tube of  
30 molten film is extruded from an upright annular die sur-  
31 rounding a blowhead, which inflates the tube, the inflated  
32 tube being cooled with externally blown air. Thereafter,  
33 the tube is collapsed and wound on two rolls. The air is  
34 trapped in the bubble by the die at one end and the take-  
35 up rolls at the other. The blends of the present invention  
36 are significant in that they exhibit sufficiently high melt  
37 strength combined with sufficiently high flow, as indicated

1 by melt index, to permit manufacture into films using this  
2 conventional blown-bubble extrusion process. The melt in-  
3 dex of the film-forming blend composition of the present  
4 invention should be in the area of about 0.5 to 15.0 gm./10  
5 min. at 190°C to maintain stability for processing in the  
6 tubular blown film apparatus.

7 The melt strength and flow characteristics of  
8 these compositions can also be beneficially employed in  
9 other methods of film manufacture such as the cast or  
10 chill-roll process, sheet extrusion or extrusion coating.  
11 Such films prepared from the compositions of the present  
12 invention are further embodiments of the present invention  
13 and offer a number of distinct properties. These films ex-  
14 hibit rubber-like properties of high resilience and recov-  
15 ery after stretching, low stress relaxation, heat shrink-  
16 ability and acceptable tear strength. These properties  
17 render these films adaptable to a wide variety of uses not  
18 possible with conventional polyolefin plastics films.

19 Elasticity of films prepared in the present in-  
20 vention is indicated by an Elastic Modulus value (at 125%  
21 extension, 5in./min. crosshead speed) of about 250 to 400  
22 psi, with a value of about 250 psi having been found high-  
23 ly desirable. The films prepared from the compositions of  
24 the present invention have ultimate elongation values of  
25 about 100% to 300% and are also heat shrinkable, with 75%  
26 to 100% recovery of properties after heat shrinking 5 sec-  
27 onds at 100°C.

28 Films prepared from the compositions of the pres-  
29 ent invention are a further embodiment thereof and offer a  
30 desirable combination of properties in the unoriented and  
31 oriented states. Unoriented films have high resilience,  
32 recovery after stretching and low stress relaxation. Uni-  
33 axial orientation of the film will result in a second state  
34 also having high elasticity and recovery. The films also  
35 offer the advantage of being heat shrinkable. Exposure of  
36 an oriented film to heat results in a return to the unori-  
37 ented state and the original elastic properties.

1 These properties render these films useful for a variety  
2 of wrapping, packaging and electrical insulation applica-  
3 tions.

4 Preferred film-forming compositions are those  
5 containing EPM or EPDM elastomers having at least 60 weight  
6 percent ethylene and a molecular weight sufficient to pro-  
7 vide a Mooney viscosity of about 50 ASTM D 1646 (ML 1 + 8  
8 at 127°C). Preferred ethylene-vinyl acetate copolymers  
9 are those containing about 14% to 28% by weight vinyl ace-  
10 tate. Aromatic, naphthenic or paraffinic hydrocarbon plas-  
11 ticizer oils may be used. Paraffinic and naphthenic grades  
12 are commonly lighter in color and lower in odor and there-  
13 fore preferable. Aromatic oils are generally more compati-  
14 ble with other components and exhibit less surface migra-  
15 tion when used at high percentages.

16 Calcium carbonate is an optional material for  
17 use in the compositions of the present invention and func-  
18 tions chiefly as a filler to reduce component cost. It  
19 may be used in fairly substantial amounts, up to about 30  
20 parts by weight. It has been found useful in reducing film  
21 blocking, and it will impart an off-white cloudy appearance  
22 to the film. Calcium carbonate will also reduce tackiness  
23 in the finished film product.

24 Film processing slip agents or abherents are op-  
25 tional but preferable components of the compositions of  
26 the present inventions. These materials are well known in  
27 the art and are commonly employed in film manufacture as  
28 processing aids. Numerous materials are suitable but  
29 stearic acid and stearic acid derivatives such as calcium  
30 or zinc stearate or stearamide are particularly preferred.  
31 Other suitable abherents include the C<sub>12</sub>-C<sub>22</sub> fatty acids  
32 and fatty acid amides and metal soaps, such as erucamide,  
33 silicones and natural and manufactured waxes such as gly-  
34eryl and glycol stearates, as well as inorganic abherent  
35 materials.

36 Preferred proportions for preparing the blends of  
37 the present invention are (a) 25-30 parts by weight of EPM

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1 or EPDM; (b) 45-55 parts by weight of ethylene-vinyl ace-  
2 tate copolymer; (c) 18-22 parts by weight of hydrocarbon  
3 oil and about 1.0% by weight of abherent, especially stear-  
4 ic acid.

5 For a composition containing calcium carbonate  
6 filler, the preferred proportions are (a) about 20-25 parts  
7 by weight of EPM or EPDM; (b) 15-20 parts by weight of hy-  
8 drocarbon oil; (c) 25-40 parts by weight of ethylene-vinyl  
9 acetate copolymer; (d) 20-25 parts by weight of calcium  
10 carbonate; and (e) about 1.0% by weight of stearic acid.

11 The invention is further illustrated by the fol-  
12 lowing examples which are not to be considered as limita-  
13 tive of its scope. Parts reported are by weight.

14 Example 1

15 Films were prepared and evaluated as set forth  
16 in Table 1, which reports Examples 1-A to 1-G. Materials  
17 used are identified below:

18 "EPDM A" is an EPDM containing 64 weight percent  
19 ethylene, 3.4% ethylidene norbornene and having a Mooney  
20 viscosity of 50 (ML 1+ 8 at 127°C).

21 "Flexon 785" is a naphthenic rubber compounding  
22 oil, ASTM D 2246 Type 104A having an approximate viscosity  
23 in Saybolt seconds at 210°F of 80.

24 "EPDM B" is an oil extended EPDM consisting of  
25 75 parts by weight of paraffinic rubber processing oil  
26 with 100 parts of a high molecular weight EPDM containing  
27 66% ethylene and having an overall Mooney viscosity of 45  
28 (ML 1 + 8 at 127°C).

29 EVA represents ethylene-vinyl acetate copolymer.  
30 VA represents vinyl acetate.

31 MI represents Melt Index measured at 190°C ac-  
32 cording to ASTM D-1238, Condition E.

33 "Flexon" is a trademark for petroleum oils mar-  
34 keted, respectively by Exxon Chemical Company and Exxon  
35 Company, U.S.A.

36 "LD 401" is a product of Exxon Chemical Company;  
37 "UE 632" and "UE 621" are products of U.S.I. Chemicals and



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1 "Elvax 265" is a product of DuPont.

2 All films reported in the tables below were produced  
3 by the blown-bubble extrusion process as described herein-  
4 above. Film Tensile Set is a measure of the degree of  
5 elastic recovery of the films. Low values indicate more  
6 complete recovery.

TABLE I

	1-A	1-B	1-C	1-D	1-E	1-F	1-G
1							
2							
3 EPDM A	34	48	48	--	--	--	--
4 OI1 (Flexon 785)	15	21	21	--	--	--	--
5 EPDM B	--	--	--	49	49	49	49
6 EVA Copolymer, 9% VA, 3.4 MI (LD-601)	50	30	--	50	--	--	--
7 EVA Copolymer, 14% VA, 7.5 MI (UE-632)	--	--	--	--	50	--	--
8 EVA Copolymer, 18% VA, 2.5 MI (UE-621)	--	--	30	--	--	50	--
9 EVA Copolymer, 28% VA, 3.0 MI (Elvax 265)	--	--	--	--	--	--	50
10 Stearic Acid	1	1	1	1	1	1	1
11 Melt Index @ 190°C, g/10 min	1.6	1.2	1.9	1.3	7.0	3.6	3.8
12 (ASTM D 1238, Condition E)							
13 Film Tensile Set, 100% Elongation, ASTM D412							
14 Machine Direction, (%)	20	11	10	11	12	13	17
15 Transverse Direction, (%)	24	13	18	13	11	19	22

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1  
8  
1

1 Example 2

2 Additional films were prepared as in Example 1.  
3 Elastic Modulus Melt Index and Degree of Oil Migration were  
4 evaluated. The compositions and results are in Table II.

5 LDPE represents low density polyethylene. Ex-  
6 amples 2-A and 2-D are included for the purpose of compari-  
7 son.

8 "EY 901", "UE 631" and "UE 645" are products of  
9 U.S.I. Chemicals.

1

2

3 EPDM A

4 OI1 (Flexon 815)

5 Stearic Acid

6 LDPE, 7.2 MI (LD-605)

7 EVA Copolymer, 14% VA, 7.5 MI (UE-632)

8 EVA Copolymer, 40% VA, 7.5 MI (EY-901)

9 LDPE, 2.5 MI (LD-106)

10 EVA Copolymer, 9% VA, 3.4 MI (LD-401)

11 EVA Copolymer, 19% VA, 2.5 MI (UE-631)

12 EVA Copolymer, 28% VA, 3.0 MI (UE-645)

13 Vinyl Acetate Content (% final blend)

14 Melt Index @ 190°C, g/10 min (ASTM D 1238)

15 (Condition E)

16 Elastic Modulus @ 125% extension

17 5 in/min crosshead speed (psi)

18 Degree of Oil Migration to Surface

TABLE II

	2-A	2-B	2-C	2-D	2-E	2-F	2-G
3	28	28	28	28	28	28	28
4	21	21	21	21	21	21	21
5	1	1	1	1	1	1	1
6	50	50	50	50	50	50	50
7	50	50	50	50	50	50	50
8	50	50	50	50	50	50	50
9	50	50	50	50	50	50	50
10	50	50	50	50	50	50	50
11	50	50	50	50	50	50	50
12	50	50	50	50	50	50	50
13	0	7	20	0	4.5	9.5	14
14	3.1	11.5	13.2	2.0	2.8	5.9	6.5
15	NA	250	160	NA	420	260	260
16	High	Low	None	High	Moderate	None	None

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1 Example 3

2 Additional films were prepared and evaluated as  
3 in Example 2 and are reported in Table III. Examples 3-A  
4 and 3-D are for the purpose of comparison.

1

2

TABLE III

	3-A	3-B	3-C	3-D	3-E	3-F	3-G
3 EPDM B	49	49	49	49	49	49	49
4 Stearic Acid	1	1	1	1	1	1	1
5 LDPE, 7.2 MI (LD-605)	50	--	--	--	--	--	--
6 EVA Copolymer, 14% VA, 7.5 MI (UE-632)	--	50	--	--	--	--	--
7 VAE Copolymer, 40% VA, 7.5 MI (EY-901)	--	--	50	--	--	--	--
8 LDPE, 2.5 MI (LD-106)	--	--	--	--	--	--	--
9 EVA Copolymer, 9% VA, 3.4 MI (LD-401)	--	--	--	50	--	--	--
10 EVA Copolymer, 18% VA, 2.5 MI (UE-621)	--	--	--	--	50	--	--
11 EVA Copolymer, 28% VA, 3.0 MI (UE-645)	--	--	--	--	--	50	--
12 Vinyl Acetate Content (% Final blend)	0	7	20	0	4.5	9	14
13 Melt Index @ 190°C, g/10 min (Cond. E)	0.57	6.6	5.4	0.41	1.3	3.6	2.8
14 Elastic Modulus @ 125% Extension	NA	280	110	NA	390	330	230
15 in/min crosshead speed (psf)	Moderate	None	None	Moderate	None	None	None
16 Degree of Oil Migration to Surface							

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HAT WE CLAIM IS:

1. A film-forming thermoplastic elastomeric blend composition characterized by a blend of:
  - (a) about 25 to 55 parts by weight of an EPM or EPDM elastomer having an ethylene content of from about 55 to 70 weight percent;
  - (b) about 35 to 55 parts by weight of a thermoplastic ethylene-vinyl acetate copolymer having a vinyl acetate content of about 9 to 40% by weight; and
  - (c) about 15 to 25 parts by weight of a normally liquid hydrocarbon process oil, the oil being an aromatic, highly aromatic, naphthenic or paraffinic process or extender oil, the blend composition containing at least 4.5% by weight vinyl acetate based upon the total weight of the blend composition and the blend composition having a melt index at 190°C of about 0.5 to 15 gm./10 min.
2. A composition according to claim 1 further characterized by (d) about 0 to 30 parts by weight of calcium carbonate filler and (e) about 0.5 to 2.0% by weight of a film processing adherent based on the total composition.
3. A composition according to claims 1 or 2 characterized in that said (a) component is an EPM elastomer.
4. A composition according to claims 1 or 2 characterized in that said (a) component is an EPDM elastomer, and the diene is ethylidene norbornene.
5. A composition according to claims 1-4 characterized in that said (b) component has a vinyl acetate content of about 14% to 18% by weight.
6. A composition according to claims 1-5 characterized in that (c) component is an aromatic or highly aromatic hydrocarbon oil.

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7. A composition according to claims 2-6 characterized in that said (e) component is stearic acid.

8. A composition according to any of the preceding claims characterized in that there is present about 25 to 30 parts by weight of said (a) component; about 45 to 55 parts by weight of said (b) component; about 18 to 22 parts by weight of said (c) component; and further comprising about 1% by weight of stearic acid based on the total weight of the blend composition.

9. A composition according to any of the preceding claims characterized in that there is present about 20 to 25 parts by weight of said (a) component; about 15 to 20 parts by weight of said (b) component; about 25 to 40 parts by weight of said (c) component; about 20 to 25 parts by weight of said (d) component and about 1% by weight of said (e) component.

10. A film characterized in that it is produced from the composition of any of the preceding claims.

11. A film characterized in that it is produced from the composition of any of the preceding claims by the blown-bubble extrusion method.

12. A film characterized in that it is produced from the composition of any of the preceding claims by the cast or chill roll film extrusion method.

13. A film according to claim 11 characterized in that it has an Elastic Modulus of about 250 to 400 psi.